

CHANGES IN HYDROGEN UTILIZATION WITH TEMPERATURE DURING DIRECT COAL LIQUEFACTION

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INTRODUCTION

The role of hydrogen is of particular interest in direct coal-conversion chemistry. The presence of high pressure gaseous hydrogen is beneficial in virtually any direct conversion experiment, even under low severity conditions where the net hydrogen incorporation is nil. The hydrogen chemistry is extremely important in process design due to the large impact of hydrogen consumption on the process economics. An ideal process would consume a minimum of hydrogen while breaking the coal into soluble fragments. A reliable means of monitoring the major pathways of hydrogen utilization, in contrast to only measuring net hydrogen consumption, would be very useful for process optimization. The goal of this work was to develop an analytical approach for quantitatively distinguishing hydrogen consumed in hydrogenation from that utilized to stabilize thermolysis fragments.

The current view on the involvement of hydrogen in coal liquefaction is that it is consumed in direct hydrogenation and in the "capping" of thermolysis fragments.¹ In the capping mode, the hydrogen may be transferred by means of solvent intermediates such as hydroaromatics. The direct hydrogenation of aromatics is reasonably well understood, but the mechanism of hydrogen transfer is less clear. Upon homolytic thermolysis of a labile bond in the feed slurry, two free radicals are formed, which then stabilize by abstraction of hydrogen from nearby groups, by rearrangement, or by coupling. Rearrangement and coupling reactions of radicals can often result in hydrogen being eliminated from the fragment rather than consumed by it. In the complex, high molecular weight, slurry environment, all these routes to radical stabilization are accessible.

If coals were simple solid hydrocarbons (C_xH_y) without mineral matter or heteroatoms, there would be little interest in liquefaction, since a major goal of liquefaction is the removal of N, O, S, and mineral matter from the coal. Heteroatom removal is one of the most important roles for hydrogen in coal liquefaction, and it can be considered a subcategory of the thermolysis stabilization reactions just described.

Experimental evidence shows that the simple picture of bond thermolysis/radical stabilization outlined above is a gross oversimplification of direct coal conversion chemistry. In liquefaction experiments under an atmosphere of deuterium, the label is found in virtually all positions in the product. Positions α to aromatic rings are usually preferred, but a significant portion of the label appears in aromatic positions.² The methane produced also contains significant concentrations of deuterium, and dideuteromethane often predominates.³ The presence of coal strongly catalyzes isotopic scrambling in a number of model systems.⁴ These results are difficult to rationalize using the very simple model for hydrogen utilization.

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Also, considerable conversion of coal to soluble products can occur under mild conditions where no net hydrogen is consumed. In this case, any hydrogen consumed must be compensated for within the slurry system. The ability of coal to act as a hydrogen donor is well documented.⁵

In a realistic direct conversion process, the distinction between coal and solvent is somewhat artificial. The slurry vehicle in a continuous unit operating at a steady state is a subfraction of the product from a previous cycle, making it impossible to clearly distinguish "solvent" from product oil in the reactor effluent. There is substantial evidence that solvent quality is enhanced by inclusion of certain high molecular weight components.⁶ The solvent in these systems is intimately involved as a reactant and not as a neutral diluent. Thus, it may be preferable to consider the total feed slurry as a reactant mixture rather than as coal plus solvent.

Formulation of Analytical Approach

The fact that it is difficult to understand the detailed, molecular-level mechanism of hydrogen incorporation in complex liquefaction systems does not preclude improvements in understanding the net chemistry. It is reasonable to assume that hydrogen consumption will involve either hydrogenation or bond scission reactions. Conversely, both aromatization, the reverse of hydrogenation, and condensation, the reverse of bond scission, are potential sources of hydrogen. Exchange and isomerization reactions do not affect the net hydrogen balance.

Since stoichiometries of the two classes of hydrogen incorporation reactions differ, it is possible to construct a model that discriminates between the two. Such a model requires determination of the change in total hydrogen, the change in aromatic hydrogen, and the number of hydrogens incorporated during bond cleavage. The relationship between these quantities will be expressed as

$$\Delta_{\text{Total}}^{\text{H}} = \Delta_{\text{Cleavage}}^{\text{H}} + \Delta_{\text{HYD}}^{\text{H}} \quad (1)$$

where $\Delta_{\text{Total}}^{\text{H}}$ is the total change in hydrogen,

$\Delta_{\text{Cleavage}}^{\text{H}}$ is the hydrogen consumed in bond cleavage, and

$\Delta_{\text{HYD}}^{\text{H}}$ is the hydrogen consumed in hydrogenation of the slurry.

This relationship describes only the reactions of hydrogen with the organic portion of the feed slurry. Focusing attention only on the organic reactions alleviates, to some extent, problems in the interpretation of total hydrogen balances. In total hydrogen balance calculations, it is impossible to distinguish H_2S and H_2O arising from organic reactions from those produced by inorganic sources in the coal. Although NH_3 presents less of a problem, some ammonia may be liberated from certain clays upon heating. The analytical problems associated with measuring small changes in the huge excess of gaseous hydrogen normally present under direct conversion conditions are also eliminated, since only carbonaceous products are analyzed.

Assuming that the total change in hydrogen ($\Delta_{\text{Total}}^{\text{H}}$) can be determined by classical elemental analysis, then a method for measuring either the hydrogen consumed upon hydrogenation or bond cleavage is needed to use Equation 1. Since no satis-

factory method is available to count bonds before and after reaction in a coal liquefaction system, it is necessary to concentrate on determination of $\Delta_{\text{H}}^{\text{H}}_{\text{H}}^{\text{H}}$. Although research efforts are underway to determine hydrogen speciation in solid coals, it is doubtful that any of the current methods are sufficiently quantitative for the present purpose.⁷ One analytical tool that can be applied with reasonable confidence to both solids and liquids is ^{13}C nuclear magnetic resonance (NMR). Fortunately, it provides an indirect measurement of the hydrogen consumed in hydrogenation. Hydrogenation of organics results in incorporation of one hydrogen for every carbon reduced. Thus if a sample is hydrogenated without structural changes from an aromaticity of 0.80 to 0.70, then 10 carbons per 100 have been reduced and 10 hydrogens have been incorporated. The ratio of 1 hydrogen per carbon reduced does not hold exactly if there is significant reduction of aromatic nitrogen heterocycles, but the 1:1 stoichiometry is a good approximation if these reactions can be neglected. Combining elemental analysis and ^{13}C NMR data, the amount of hydrogen consumed in bond scission can be determined by difference.

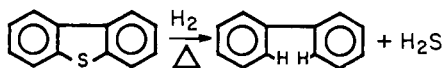
Bond scission can be further divided into three categories, those resulting in (1) heteroatom elimination as H_2O , H_2S , or NH_3 , (2) $\text{C}_1\text{-C}_4$ hydrocarbon gas production, and (3) breakdown of the coal matrix to yield nonvolatile (solid or liquid) products.

$$\Delta_{\text{Cleavage}}^{\text{H}} = \Delta_{\text{NOS}}^{\text{H}} + \Delta_{\text{C}_1\text{-C}_4}^{\text{H}} + \Delta_{\text{Matrix}}^{\text{H}} \quad (2)$$

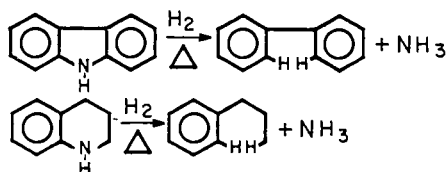
If a quantitative measure of the hydrogen used in these three bond scission modes can be obtained, it would be very useful in monitoring changes in liquefaction chemistry with reactor conditions such as temperature, pressure, catalyst, residence time, and feed composition.

In many respects, the direct conversion reactor is an inefficient coal gasifier that converts 5-20% of the coal to $\text{C}_1\text{-C}_4$ hydrocarbons while producing a by-product liquid (20-80%). Since $\text{C}_1\text{-C}_4$ hydrocarbon gases usually constitute a significant product stream, they must be carefully analyzed if the approach just described is to succeed. If accurate gas analyses are available and it is assumed that all hydrocarbon gases are generated by cleavage of alkyl substituents from aromatics, an estimate of the hydrogen consumed in gas production can be obtained. One mole of hydrogen is incorporated for every mole of light gas formed.

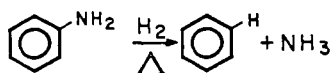
The most difficult term to evaluate in Equation 2 is $\Delta_{\text{NOS}}^{\text{H}}$, the hydrogen consumed in heteroatom removal. The difficulty arises because of the variety of heteroatomic structures present and the different hydrogen stoichiometries involved in their elimination. If the organic sulfur in the feed slurry can be assumed to be primarily thiophenic, two hydrogens are incorporated per sulfur removed as H_2S :



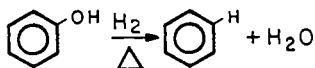
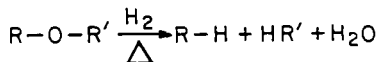
Removal of heterocyclic nitrogen proceeds through the fully hydrogenated nitrogenous ring system (5- or 6-membered).⁸ There is a net incorporation of one hydrogen per nitrogen eliminated:



If amine functions exist in the feed, elimination of one amine nitrogen actually decreases the hydrogen content by one hydrogen:



If the discussion is confined to bituminous coals, the majority of the organic oxygen will reside in either phenolic or ether structures.⁹ Removal of ether oxygen results in the net incorporation of two hydrogens per oxygen removed, and removal of phenolic oxygen results in no net change in hydrogen:



Under mild conditions where only minimal heteroatom removal occurs, the question of hydrogen stoichiometry is unimportant. However, under severe processing conditions significant heteroatom reduction can occur and an average stoichiometry must be assigned. For the present purposes, it has simply been assumed that on the average one hydrogen is incorporated into the carbonaceous product per heteroatom removed from the organic portion of the feed slurry.

Combining Equations 1 and 2 yields

$$A_{\text{Total}}^{\text{H}} = A_{\text{HYD}}^{\text{H}} + A_{\text{C}_1\text{-C}_4}^{\text{H}} + A_{\text{NOS}}^{\text{H}} + A_{\text{Matrix}}^{\text{H}} \quad (3)$$

The term $A_{\text{Matrix}}^{\text{H}}$ can be determined by difference. Using Equation 3, only elemental analyses, carbon aromaticities, and quantitative gas analyses are required to partition the hydrogen consumption into that used in gas production, hydrogenation, heteroatom removal, and matrix bond cleavage. In reactions producing significant CO or CO₂, a correction must be applied to Equation 3, but in the experiments described below, both CO and CO₂ were negligible.

Experimental

The model just described was initially applied to a single steady-state period 800 hours into a long-term liquefaction experiment (FB-62) on the 400 lb/day coal liquefaction unit at PETC.¹⁰ The unit was operated at 450°C under 4,000 psig H₂ pressure while feeding a 35% slurry of West Virginia (Ireland Mine) HvAb coal in centrifuged liquid product from a previous period of the run. Subsequently, a series of liquefaction runs on a 10 lb/day continuous coal liquefaction unit at PETC was investigated.¹¹ In the latter unit, a 40% coal slurry prepared from Homestead, Kentucky, HvAb coal and centrifuged liquid product produced from the same coal in the 400 lb/day unit was liquefied under 2000 psig H₂ at programmed temperatures between 375°C and 450°C. More recently, two series of experiments have been studied involving liquefaction of reactive (Illinois No. 6) and refractory (Blacksville No. 2) coals in the presence of SRC-II distillate in a stirred autoclave under 2000 psig H₂ over the temperature range 300°C to 450°C.

Elemental analyses of the organic material in the feed slurries were obtained from separate analyses of the vehicles and coal. Elemental analyses of the vehicles were done by classical microanalytical procedures, including direct oxygen determinations. The feed coals were analyzed by both microanalytical and standard

ASTM coal methods for moisture, ash, and sulfur forms. Product gases were analyzed by low resolution mass spectrometry of grab samples and gas chromatography. The products were split by Soxhlet extractions into methylene chloride soluble and insoluble fractions, which were then analyzed separately. The carbon aromaticity change across the reactor was determined by ^{13}C NMR, using the CP/MAS technique on the insoluble fractions and high resolution ^{13}C NMR in CD_2Cl_2 for the soluble fractions.

Results and Discussion

A comparison of the net changes in composition of the feed slurry and total product for Run FB-62 on the 400 lb/day unit is presented in Table 1. Combined with the gas make (8 wt% maf), the data in Table 1 allow application of Equation 3 to determine the modes of net hydrogen utilization in the reactor shown in Table 2.

Table 1. Analysis of feed slurry and total product, Run FB-62.

	Elemental Analyses (atoms/100 carbon atoms)					Carbon Aromaticity (f_a)
	C	H	N	O	S	
Feed Slurry	100	96	1.3	4.3	0.8	0.70
Total Product	100	106	1.3	2.6	0.6	0.67
Net Change	---	+10	0	-1.7	-.2	-0.03

Table 2. Net hydrogen utilization in Run FB-62.

Mode of Hydrogen Utilization	H Consumed/100 C
Gas Make	2
Heteroatom Elimination	2
Hydrogenation	3
Matrix Cleavage	3
Total	10

The results indicate nearly equal consumption of hydrogen by each of the four pathways considered at 450°C in the 400 lb/day unit.

Products produced at various temperatures in the 10 lb/day unit were then analyzed to determine if this analytical approach would detect changes in hydrogen utilization as reactor conditions changed. A plot of total product aromaticity vs. programmed reactor temperature is shown in Figure 1. The actual reactor temperatures vary somewhat from the programmed temperatures, but for simplicity, Figure 1 uses the programmed temperature. The three data points at each temperature correspond to three different hydrogen flow rates (80, 103, and 125 SCF/hr). The spread in values at a given temperature arises from experimental errors in the f_a determination and from sampling errors, as well as any real effect of hydrogen flow rate. Current work is being directed toward reduction of the data scatter. In this work the data points are all presented with no statistical justification of the indicated curve. Since other analyses show little, if any, effect of hydrogen flow rate in this range, the f_a values at each temperature can be averaged to yield an estimate of the actual best value indicated on the plot as a star.

The horizontal dashed line in Figure 1 indicates the carbon aromaticity of the slurry feed, obtained as a weighted average of the aromaticities of the slurry components. At low temperatures, where no chemical reaction takes place, the reactor would simply be mixing the slurry components. At the other extreme in temperature (450°C), the liquid product aromaticity is expected to again approximate the value for the solvent, since this is a requirement for steady-state recycle operation. Figure 1 indicates that the total aromaticity has nearly returned to the slurry line at 450°C, and the liquid product (CH₂Cl₂ solubles) has an aromaticity (0.69) that compares well with that of the vehicle (0.68). The most distinctive and surprising feature in Figure 1 is the apparent minimum in the carbon aromaticity at 400°C. This minimum suggests very significant changes in product hydrogen distribution upon going from 375°C to 400°C. This change is observed, although there is still little net hydrogen incorporation, no gas production, and relatively little heteroatom elimination at these temperatures. The only heteroatom lost under these conditions is oxygen, and part of this apparent loss may well be due to simple water loss rather than elimination of organic oxygen.

Applying the model to the average f_a data in Figure 1 results in the hydrogen utilization pattern shown in Table 3. As anticipated, little net hydrogen chemistry has occurred at 375°C. The only directly measurable change is the loss of one oxygen atom per 100 carbon atoms, requiring one hydrogen from matrix bond formation for balance. At 450°C, a hydrogen utilization profile much like that observed for Run FB-62 in Table 3 would be expected, and in general, that is what is found. The only difference is that the net hydrogenation is apparently less in the smaller 10 lb/day reactor that was operated at the lower hydrogen pressure. The term "apparently" should be stressed, since the absolute accuracy of f_a measurements on such samples is probably no better than ± 0.03 . At 400°C, Table 3 indicates a significantly higher consumption of hydrogen by hydrogenation, 7 hydrogens/100 carbons, while the total net hydrogen incorporation is only 3 hydrogens/100 carbons. Since 2 hydrogens/100 carbons are consumed in heteroatom removal, this indirect analysis indicates consumption of 9 hydrogens/100 carbons in the 400°C slurry, while elemental analysis indicates an incorporation of only 3 hydrogens/100 carbons overall. The model then forces assignment of a negative value to matrix cleavage consumption, implying that the net change in number of bonds across the reactor is an increase. This suggests that under these conditions, internal condensation of the slurry components is producing hydrogen that compensates for that consumed in bond cleavage, heteroatom removal, and hydrogenation. It must be emphasized that this treatment considers only net chemistry, making it impossible to determine if the internally produced hydrogen or the hydrogen atmosphere provides the consumed hydrogen.

Table 3. Hydrogen utilization during liquefaction of Homestead, Kentucky, coal in the 10 lb/day unit.

Mode of Hydrogen Consumption	Hydrogens Consumed Per 100 Carbons in Feed		
	375°C	400°C	450°C
Gas Make	0	0	4
Heteroatom Removal	1	2	4
Hydrogenation	0	7	1
Matrix Cleavage	-1	-6	3
Total	0	3	12

Table 3 indicates that as the temperature of the reactor increases from 400°C to 450°C, the total hydrogen incorporation per 100 carbon atoms increases dramatically from 3 to 12, but the net consumption in hydrogenation actually decreases from 7 to 1. This effect is probably due to increasing hydrogen production via

aromatization with increasing temperature. This is not unexpected, since low temperatures tend to favor hydrogenation, while high temperatures favor aromatization. Higher temperatures also tend to favor thermolysis over hydrogenation, and this expectation is also confirmed in Table 3, where the net bond-breaking consumption (gas make, heteroatom removal, and matrix cleavage) changes from -4 hydrogens/100 carbons at 400°C to +11 hydrogens/100 carbons at 450°C. However, even at 450°C, only 3 hydrogens/100 carbons are consumed in breaking down the slurry matrix bonds. This indicates that bond breaking predominates over condensation by only about 1.5 bonds/100 carbons.

Using the approach outlined, a reasonable picture of the changes in hydrogen utilization with temperature emerges. At low temperature (375°C), physical changes and minor internal hydrogen redistribution occur with little net hydrogen chemistry and no net consumption. At 400°C, there is still only a small hydrogen consumption, but there is also evidence of significant internal hydrogen chemistry, with hydrogenation and condensation proceeding to approximately the same degree. At high liquefaction temperatures, a more conventional view of hydrogen utilization emerges, significant net consumption being utilized primarily in bond cleavage reactions, gas make, heteroatom removal, and matrix breakdown.

An additional series of autoclave experiments on the liquefaction of Illinois No. 6 and Blacksville No. 2 coals is currently being investigated to determine if this approach can distinguish differences in hydrogen utilization between coals of different reactivity over the temperature range 300°C to 450°C. Although analyses of these runs are not yet complete, preliminary results indicate there are distinct differences between the coals in the product aromaticity versus temperature relationship.

Although the approach presented appears to be useful on the basis of the results accumulated to date, a discussion of potential problems is appropriate. Analytical errors associated with the various measurements and the assumptions of the model both contribute to uncertainty in the results. The NMR determination of f_a is a prime source of error. For this number to have any utility, all the feed and product carbons must be observed and carefully quantified. The problem of observing all of the carbon in the soluble material is not too serious if the "soluble" material is not colloidal or suspended. If the correct NMR parameters are used, the largest source of error is then in the integration of peak areas. The problem of quantitatively determining f_a for the insoluble fractions, which requires the ^{13}C -CP NMR technique, is more serious. This technique will not observe liquid-like entrapped material and may not observe carbons that are too far removed from hydrogen for the efficient transfer of polarization. The lower inherent resolution of the solid phase NMR spectra also introduces a larger error in measurement of overlapping peak areas. Another potential source of error is the quantitative determination of gas yield and composition. This measurement is important due to its large impact on both total hydrogen consumption and net product aromaticity. The determination of organic oxygen in coal and coal-derived products is always a problem, and errors in this determination translate directly into errors in hydrogen in heteroatom removal. The determination of organic sulfur in the feed slurry requires distinguishing between organic and mineral sulfur in the coal.

Conclusions

The approach outlined yields a rather detailed description of the net utilization of hydrogen during direct liquefaction, partitioning it into contributions from gas generation, heteroatom removal, hydrogenation, and matrix breakdown. Preliminary results indicate that internal hydrogen reorganization, with little consumption, predominates at low temperatures, with hydrogenation being compensated for by the hydrogen liberated in condensations. As the temperature is increased, bond cleavage reactions and aromatization reactions appear to become more important,

and the net hydrogen consumption increases. Additional studies of the assumptions in the model and of uncertainties in the required analytical data are needed to critically evaluate the utility of this approach.

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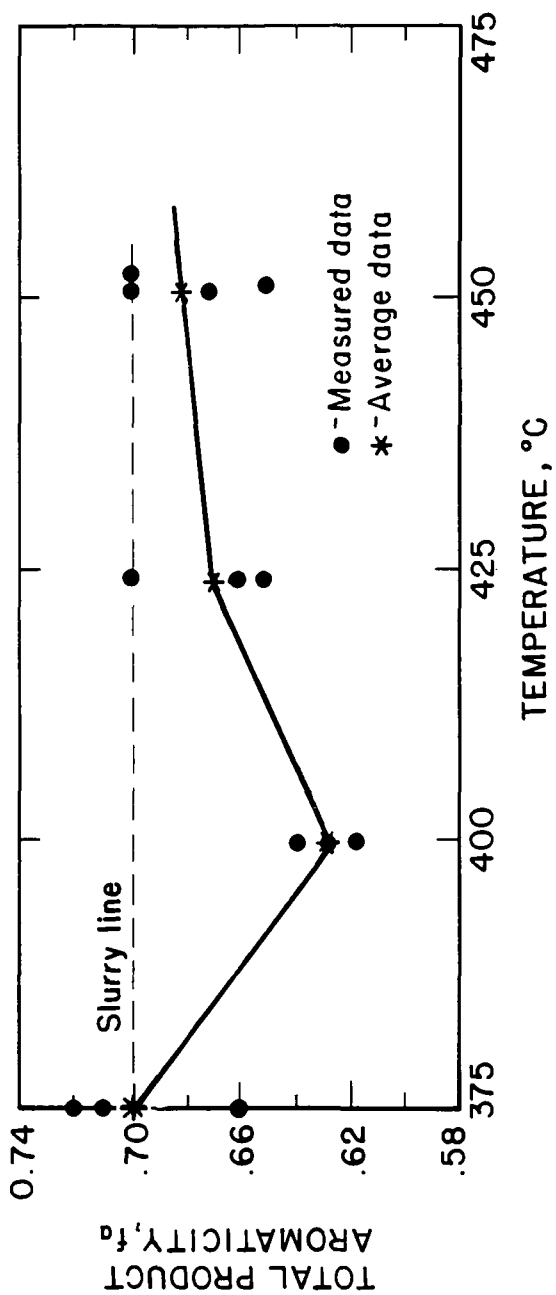


Figure 1 - Dependence of total product aromaticity on temperature.